

Appl. No. 10/017,420  
Amdt. dated September 2, 2003  
Reply to Office action of July 7, 2003

**Remarks/Arguments**

The invention claimed in the present application is a polyester bottle comprised of a polyester polymer that contains from up to about 0.1 wt. % of barium sulfate having an average particle size of from about 0.1 to about 2.0 microns. Surprisingly, it has been found that bottles prepared from this composition have a lower bottle-to-bottle friction compared to bottles without the barium sulfate additive, while being characterized by an absence of visible haze that is normally associated with the introduction of particulate additives in these amounts and sizes into polyester polymers used to produce bottles.

It is the Examiner's view that the claims, as presented prior to the present amendment, define an invention that would be obvious to one skilled in the art at the time the invention was made in view of the teachings of Peiffer et al ('663), alone or in combination with Peiffer et al ('054). Reconsideration and withdrawal of the rejections is respectfully requested in view of the present amendments and for the following reasons.

The Peiffer et al patents describe polyester films used in food packaging. The films, which are said to have low haze and low coefficients of friction, contain anti-blocking agents. Numerous inorganic and/or organic particles are listed as being suitable as antiblocking agents in the Peiffer et al films. The dispositive issue in this application is whether or not it would have been obvious to one skilled in the art to incorporate one of

these additives in specified quantities and particle sizes into polymers used in the production of polyester bottles.

As discussed in applicant's specification at p. 2, l. 13 through p. 3 l. 3, the addition of organic and inorganic particles to polyester film to increase "slipperiness" is well known in the prior art. In fact, Peiffer et al describes such particles in films as "customary additives" and "typical anti-blocking agents." However, as noted in applicant's specification at p. 3, l. 4-6, these additives are generally unsuitable for use in bottle production since their incorporation into the polymer causes haziness in bottle preforms, and thereby in the resultant bottles.

As explained in the enclosed materials from "A Course on PET Technology: Properties and Processing," by Dr. Saleh A. Jabarin, crystallization is influenced by various factors, in particular the cooling rate of the polymer. Specifically, if the polymer is allowed to crystallize, haze will result. Therefore, it is necessary to cool the polymer before crystallization can occur. This is not a problem with thin films such as the films disclosed in Peiffer et al since cooling to the center of the film occurs quickly. However, when manufacturing bottles, it is first necessary to manufacture a preform that is cooled before being reheated for bottle formation. If the preform, which would normally have a wall thickness of about 4 mm or more, i.e., at least 80 times the maximum thickness of the films in Peiffer et al, is not cooled to its center before crystallization occurs, haziness will result. Haziness in the preform invariably results in haziness in bottles manufactured from the preform.

Particles added to the polymer act as nucleation agents, which increase the rate of crystallization. Therefore, in most instances, the likelihood of obtaining hazy preforms and bottles is dramatically increased when even small amounts of particles are added to a preform. For example, U.S. patent 5,830,544 to Kerscher et al, discussed in applicant's specification at p. 1, l. 25 to p. 2, l. 4, discloses that addition of more than 0.005 wt. % of amorphous silicon dioxide, causes haziness in polyester bottles. To the contrary Pfeiffer et al ('663) teach at Col. 5, ll. 27-31, that preferred particles of silicon dioxide in amounts up to 5% can be added to film while still maintaining clarity.

Thus, the prior art teaches away from the addition of antiblocking agents to polyester polymers used in the production of polyester bottles. However, applicant has determined that one of the numerous blocking agents disclosed by Pfeiffer et al, when used in a particular particle size, can be added to polyester polymers at levels significantly greater than the levels disclosed by Kerscher et al to bottles with reduced bottle-to-bottle friction that are free from visual haze.

When considering the totality of knowledge available to one skilled in this particular technology, instead of picking and choosing with the benefit of applicant's disclosure, there is simply nothing in the prior art that would suggest to one skilled in the art that this result was achievable. Therefore, when applying the standard repeatedly stated by the U. S. Court of Appeals for the Federal Circuit, there is no basis for holding that the claimed invention would be "obvious" to one skilled in the art:

*In re Rouffet*, 149 F.3d 1350, 1357 (Fed. Cir. 1998): "To prevent the use of hindsight based on the invention to defeat patentability of the invention, this court requires the examiner to show a motivation to combine the references that create the case of obviousness. In other words, the examiner must show reasons that the skilled artisan, confronted with the same problems as the inventor and with no knowledge of the claimed invention, would select the elements from the cited prior art references for combination in the manner claimed."

*In re Werner Kotzab*, 217 F.3d 1365, 1371, 55 USPQ2d 1313, 1317 (Fed. Cir. 2000): "A rejection cannot be predicated on the mere identification of individual components of claimed limitations. Rather, particular findings must be made as to the reason the skilled artisan, with no knowledge of the claimed invention, would have selected these components for combination in the manner claimed."

*In re Dance*, 160 F.3d 1339, 48 USPQ2d 1635 (Fed. Cir. 1998): "To establish a prima facie case of obviousness based on a combination of the content of various references, there must be some teaching, suggestion or motivation in the prior art to make the specific combination that was made by the applicant. *In re Raynes*, 7 F.3d 1037, 1039, 28 USPQ2d 1630, 1631 (Fed. Cir. 1993)."

In this respect, and in response to the Examiner's comments, it is to be noted that neither of the Peiffer et al patents disclose addition of anti-blocking agents to polyester bottles. The statement that "Peiffer et al ('663) and Peiffer et al ('054) teach the bottle as discussed above" made at several instances in the Office Action, is contrary as to what is actually disclosed by the patents. The only reference made to bottles in either of these patents is in the '054 patent at Col. 4, ll. 60-67, which describes a prior art copolyester with no disclosed antiblocking agents that forms a suitable oxygen barrier.

The fact that it is "notoriously well known to produce bottles from polyester" is inapposite. The issue is whether it is well known to produce haze-free polyester bottles including anti-blocking agents, and in particular barium sulfate, of the defined particle

size in the defined amounts. There is no teaching in either of the Peiffer et al patents that would motivate one skilled in the art to use the Peiffer et al polymers to manufacture polyester bottles, especially when it is generally believed among those skilled in the art that the addition of such particles would result in increased crystallization rates and unacceptable haziness.

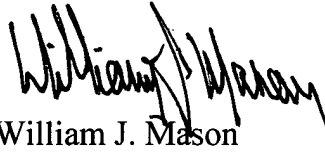
The Examiner states that applicant's allegation that the Pfeiffer et al ('663) film "is only from 4 to 50  $\mu\text{m}$ " is not accurate since Peiffer et al states at Col. 6, ll. 18-22 that the thickness of the film can vary within broad limits and depends on the intended application. The Examiner is requested to look at the next sentence which reads, "It is from 4 to 50  $\mu\text{m}$ , in particular from 5 to 45  $\mu\text{m}$ , preferably from 6 to 40  $\mu\text{m}$ ." It is respectfully submitted that the skilled artisan would interpret this unequivocal statement as calling for an upper limit of 50  $\mu\text{m}$ . Certainly, there is nothing in this sentence, particularly taken in the context of the entire patent disclosure, that would constitute a teaching, suggestion or motivation to apply the teachings to a product with a dramatically thicker wall. In fact, application of the teaching of the patent to any product other than film having a maximum thickness of 50  $\mu\text{m}$  would be contrary to the clear teaching of the patent.

The claims have been amended to better clarify the distinctions of applicant's invention over the prior art and to address the other issues raised by the Examiner.

For the forgoing reasons, and in view of the amendments to the claims, it is believed that this application now defines a patentably distinguishable invention and is

accordingly in condition for allowance. Such action is respectfully solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "William J. Mason". The signature is written in a cursive, flowing style with some loops and flourishes.

William J. Mason  
Registration No. 22,948

Date: September 2, 2003  
File No. 5540-002

**A Course**  
**on**  
**PET Technology:**  
**Properties and Processing**

**Instructor:**

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**SALEH A. JABARIN**

## 5. CRYSTALLIZATION

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Crystallization kinetics can be studied using a variety of methods including dilatometry, calorimetry, x-ray diffraction, microscopy, light scattering, depolarized light intensity, infrared spectroscopy, density and haze measurements. Among the methods most commonly used, are those based on thermodynamic properties. These include the specific volume or its reciprocal, the density and the enthalpy, which is readily measured using a differential scanning calorimeter (DSC).

### Haze<sup>(1)</sup>

Haze measurements have also been widely used to characterize optical properties of polymer films<sup>(1)</sup>. According to ASTM D 1003-59T, haze is that percentage of the transmitted light which is scattered at an angle greater than  $2.5^\circ$  from the incident beam.

Examples of variations of percent haze with crystallization times, at several temperatures, are shown below for a typical PET sheet sample.

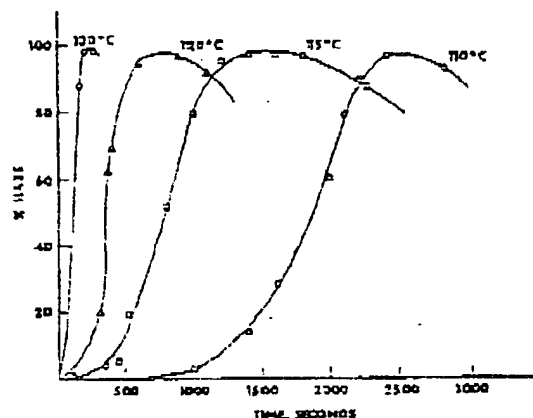


Fig. 5.1 The variation of percent haze with time of crystallization at various crystallization temperatures

At each temperature the haze first increases slowly. It then rises sharply after longer exposure times. As crystallization continues the percent haze reaches a maximum and then decreases slightly. The sharp increase in haze occurs at times when the degree of crystallinity is still quite low, as seen in this plot of percent crystallinity versus isothermal exposure time.

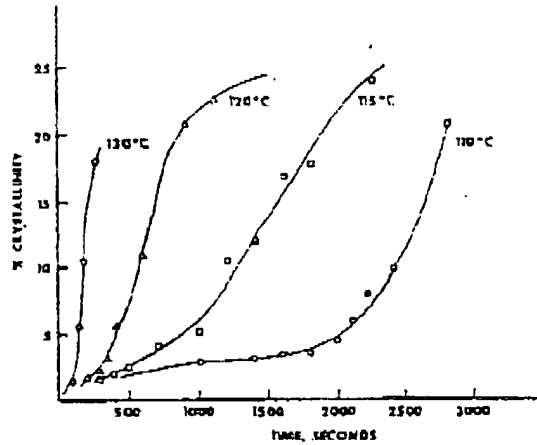


Fig. 5.2 Crystallization of polyethylene terephthalate from glassy state

The relationship between haze and degree of crystallinity is shown in this figure.

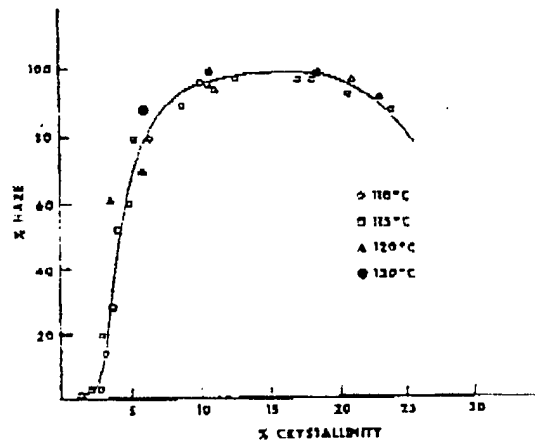


Fig. 5.3 The dependence of percent haze of PET on percent crystallinity

It is seen that percent haze exhibits a maximum, which occurs at about 15% crystallinity. This maximum and its relationship to spherulite size will be discussed later.

It is clear from this data, if the objective is to produce transparent molded parts from PET, the early stages of crystallization are very important. This is true because the development of turbidity or haze will be noticed at a small fraction of crystallinity.

The crystallization behavior of PET is determined by a number of interacting factors which include: molecular weight (intrinsic viscosity), catalyst system, polymerization conditions, cooling rate, crystallization temperature, residual stress, and moisture content.

Results and examples used to describe the above relationships have been determined primarily with the use of a differential scanning calorimeter (DSC). Samples were crystallized under isothermal and dynamic conditions after being cooled from the melt as well as heated from the glassy state. A Perkin-Elmer DSC-2 instrument was used. Samples of about 10 mg were weighed in aluminum sample holders. The calorimeter was operated with a stream of oxygen-free dry nitrogen flowing over the sample to provide an inert atmosphere. All samples which were previously dried in a vacuum oven to a moisture content of less than 0.005% were heated at a rate of 10°C/min. up to 294°C, then held at that temperature for 15 minutes to remove all previous thermal history. The isothermal crystallization conditions were reached by rapidly quenching to the desired temperature. The dynamic crystallization condition was achieved by employing programmed cooling of the sample covering the range of 5-40°C/min. During crystallization an exotherm is recorded. This exotherm permits the rate and extent of crystallinity to be monitored during the process of crystallization.

### Isothermal Crystallization<sup>(2)</sup>

During isothermal crystallization the calorimeter measures the evolution of heat as a function of time. Isotherms can be constructed by integrating the area under an exotherm according to:

$$X_t = \int_0^t \frac{dH}{dt} dt / \int_0^\infty \frac{dH}{dt} dt \quad (1)$$

where  $dH/dt$  is the rate of evolution of heat,  $t$  is the time, and  $X_t$  is the weight fraction of crystallized material at time  $t$ . In work on polymer crystallization, it is customary to represent experimental results in terms of the fraction of uncrystallized material,  $\theta_a$ .

$$\theta_a = (1-X) \quad (2)$$

This variable can be plotted as a function of time ( $\ln t$ ) to give plots called crystallization isotherms. Examples of crystallization isotherms are shown below.

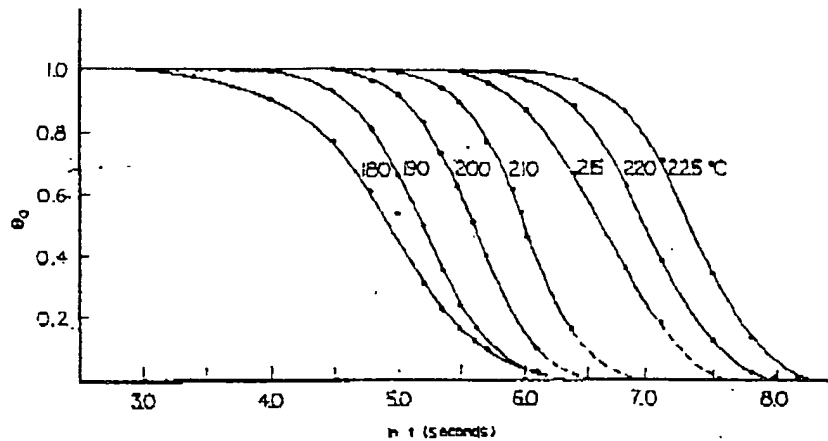


Fig. 5.4 Crystallization isotherms of Goodyear 5041 PET at 180, 190, 200, 215, and 225°C.

These isotherms generally exhibit a sigmoidal shape, which is typical of polymer crystallization behavior. In many cases, these isotherms can be superposed by shifting them horizontally along the time axis, indicating that similar mechanisms of crystallization are occurring at each temperature.

The crystallization kinetics of polymers are frequently analyzed in terms of the Avrami expression:

$$\Theta a = e^{-kt^n} \quad (3)$$

where  $\Theta a$  is the fraction of uncrystallized material,  $k$  is the kinetic rate constant,  $t$  is the time, and  $n$  is the Avrami exponent describing the mechanism of crystallization.

Values of the Avrami Exponent,  
for various types of nucleation and growth<sup>(3)</sup>

$n$	Mechanism
4	Spherulitic growth from sporadic nuclei
3	Spherulitic growth from instantaneous nuclei
3	Disk-like growth from sporadic nuclei
2	Disk-like growth from instantaneous nuclei
2	Rod-like growth for sporadic nuclei
1	Rod-like growth for instantaneous nuclei

In the Avrami expression, the kinetic rate constant, ( $k$ ), is a function of the nucleation and the growth rate. The Avrami exponent provides qualitative information about the nature of nucleation and the growth processes.

The kinetic parameters are obtained from Equation (3) by plotting the data according to:

$$\ln(-\ln \Theta a) = \ln k + n \ln t \quad (4)$$

A plot of  $\ln(-\ln \Theta a)$  versus  $\ln t$  yields a straight line whose slope is equal to  $n$ , with an intercept of  $\ln k$ . The following figure is an example of an Avrami plot obtained with data previously shown for crystallization isotherms.

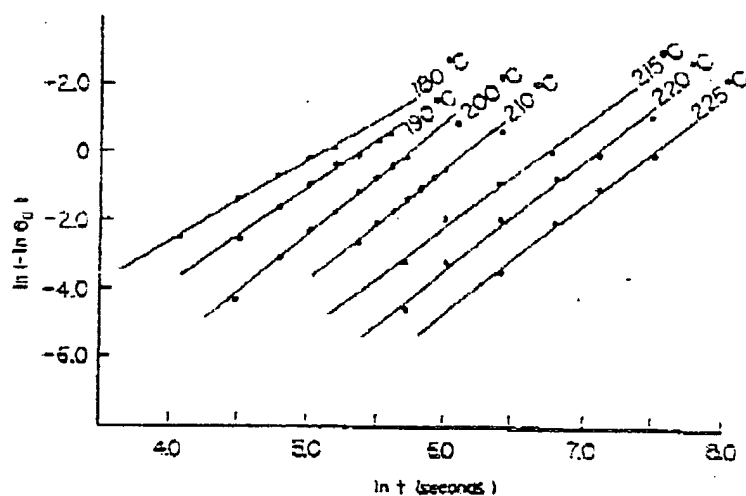


Fig. 5.5 Avrami plot of crystallization behavior of Goodyear 5041 PET at various temperatures

The table below shows examples of Avrami ( $n$ ) exponents and rate constants ( $k$ ) determined for PET resins of several molecular weights manufactured by different companies under a variety of conditions.

Table I

PET Resins

Property	Goodyear 5041	Goodyear 5041 X	Goodyear 5737 A	Celanese 4070 C	Eastman X-14829-83-1	Goodyear 3599	ICI 8-76
IV	1.04	0.83	0.72	0.68	0.61	1.0	0.88
Monomer	TPA	TPA	TPA	TPA	DMT	DMT	DMT
Catalyst system	Sb	Sb	Sb	Ti-Mn	Ti-Mn	Sb-Mn	Ti-Mn
Stabilizer additions	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus
DEG, mole %	1.0	1.7	1.4	1.7 Continuous	1.7	1.3	2.3
Polymerization process	Solid-state	Solid-state	Solid-state	Melt-phase	Solid-state	Solid-state	Melt-phase

Temp. °C	Analysis		Analysis		Analysis		Analysis		Analysis	
	n	k, sec <sup>-n</sup>	n	k, sec <sup>-n</sup>	n	k, sec <sup>-n</sup>	n	k, sec <sup>-n</sup>	n	k, sec <sup>-n</sup>
170	-	-	-	-	-	-	-	-	2	6.2x10 <sup>-7</sup>
180	3	5.0x10 <sup>-6</sup>	-	-	-	-	-	-	2	22.5x10 <sup>-5</sup>
190	3	2.5x10 <sup>-7</sup>	-	-	3	31.7x10 <sup>-7</sup>	-	-	3	0.63x10 <sup>-7</sup>
200	3	3.0x10 <sup>-8</sup>	3	10.2x10 <sup>-8</sup>	3	45.8x10 <sup>-8</sup>	3	1.86x10 <sup>-8</sup>	3	1.43x10 <sup>-10</sup>
210	3	9.2x10 <sup>-9</sup>	3	16.9x10 <sup>-9</sup>	3	44.4x10 <sup>-8</sup>	3	9.3 x10 <sup>-9</sup>	3	4.87x10 <sup>-9</sup>
215	3	1.8x10 <sup>-9</sup>	-	-	-	-	-	-	3	1.1x10 <sup>-7</sup>
220	3	5.1x10 <sup>-10</sup>	3	8.2x10 <sup>-10</sup>	3	26.6x10 <sup>-10</sup>	3	21.0x10 <sup>-10</sup>	-	1.50x10 <sup>-10</sup>
225	3	1.9x10 <sup>-10</sup>	-	-	-	-	-	-	-	34.8x10 <sup>-10</sup>

Abbreviations: IV Measured in 0.5M *o*-bromoterephthalic acid at 25°C. TPA = terephthalic acid, DMT = dimethyl terephthalate, Sb = Antimony, Ti = titanium, Mn = manganese, DEG = diethylene glycol

The rate constant,  $k$ , in Eq. (3) determines the rates of the nucleation and the growth processes which control the crystallization. It is extremely sensitive to temperature. As seen in the Table, a change of  $10^4$  is obtained for a change of crystallization temperature of 45°C in the case of Goodyear (5041) PET and  $10^3$  for a change of 50°C in the case of ICI PET samples.

These results indicate a very important feature of PET crystallization. The values of  $n$  are different for different PET samples. This indicates that the crystallization mechanism is different for different PET samples. Although the two kinds of Goodyear PET (5041 and 3599) have virtually the same molecular weight (IV = 1.0), the  $n$  and  $k$  values are significantly different. This is partly due to the secondary molecular structure brought about by the use of different polycondensation catalyst systems. The same point can be illustrated by comparing the results obtained for Goodyear 3599 and ICI PET samples. Although the Goodyear 3599 PET is of higher molecular weight (I.V. = 1.0) than the ICI PET (IV = 0.68), the crystallization rates of ICI PET are significantly lower than those of Goodyear (3599) PET. The differences can also be accounted for by the secondary molecular structure due to the polycondensation catalyst systems. Similarly, although the Eastman and Goodyear 5041X are of similar IV, the rates of crystallization of Eastman are significantly lower.

The results given in Table I show that the  $n$  values change from  $n = 3$  to  $n = 2$  at lower crystallization temperatures for the ICI and the Goodyear (3599) PET samples. This sort of behavior has been observed by other workers,<sup>(4,5)</sup> and it indicates a transition in the mechanism of crystallization. In order to elucidate the differences in growth mechanisms or differences between nucleation courses, another independent technique such as microscopy or light scattering is needed. The application of these techniques, however, requires the use of thin films.

The half-time of crystallization is used by some workers as a measure of crystallization rate. This can sometimes be misleading and result in gross errors. The explanation is as follows:

$$\text{At } t = t_{1/2} \quad \text{then} \quad \theta_a = 1/2$$

From Eq. (3), it follows that

$$k = \frac{0.69}{t_{1/2}^n}$$

In other words, the rate constant,  $k$ , is a combined function of  $t_{1/2}$  and  $n$ , and hence  $t_{1/2}$  values alone do not provide a direct means for comparing the rates for the two different processes if  $n$  is also changing. The application of  $t_{1/2}$  for determining the rate of crystallization would require a prior knowledge of  $n$ .

### Conclusions

The crystallization behavior of various polyethylene terephthalate, PET, resins varying in molecular weight and in the polycondensation catalyst systems has been investigated. The results lead to the following conclusions.

1. The crystallization rates and the mechanism of crystallization are dependent on molecular weights, temperature, and the catalyst system used during polycondensation PET.
2. The catalyst system can exhibit a greater influence in controlling the rate and mechanism of crystallization than the molecular weight of PET.
3. Among the catalyst systems investigated, a titanium-base catalyst exhibits the lowest crystallization rates, for PET of equivalent molecular weight.
4. The half time of crystallization may not be a good measure of the rate of crystallization, as often believed, if the mechanism of crystallization is also varying, that is, the Avrami exponent  $n$  is also changing.

### Dynamic Crystallization<sup>(6)</sup>

Crystallization behavior of PET can also be measured while samples are being cooled from the melt or heated from the glassy state. This dynamic crystallization is more difficult to analyze theoretically than isothermal crystallization, but it more closely simulates conditions experienced by a material during production and fabrication.

Previously described work investigated isothermal crystallization kinetics of PET samples cooled from the melt. This work was undertaken to study the dynamic crystallization behavior of PET, at a variety of constant rates of cooling from the melt. Specifically the objectives were: (a) Determine the effects of cooling rates on the crystallization behavior of PET. (b) Compare the results of isothermal and nonisothermal conditions and determine how the various factors (i.e. structural and physical) affect each case. (c) Determine the minimum cooling rate required to prevent detectable crystallinity from developing in PET samples of various molecular weights and polycondensation catalysts systems.

Materials used for isothermal crystallization studies were also used for dynamic investigations. For this work samples were cooled from the melt at rates from 5 to 40°C/min. During dynamic crystallization the calorimeter measures the rate of evolution of heat as a function of time. Crystallization isotherms are constructed by integrating the areas under the exothermic peaks according to the following equation:

$$X_t = \int_0^t \frac{dH}{dt} dt \quad \int_0^{\infty} \frac{dH}{dt} dt \quad (1)$$

where  $dH/dt$  is the rate of evolution of heat,  $t$  is the time, and  $X_t$  is the weight fraction of crystallized material at time  $t$ .

The degree of crystallinity achieved in the dynamic crystallization case is calculated from:

$$X = \frac{\Delta H_c}{\Delta H} \quad (5)$$

where  $\Delta H_c$  is the measured heat of crystallization.  $\Delta H$  is the heat of crystallization of completely crystalline PET = 20.2 cal/g (7). The heat of crystallization is calculated from the total area under the exotherm using standard Perkin-Elmer software.

Typical DSC curves obtained during the dynamic crystallization of PET are shown below for cooling rates of 5 and 20°C/minute. It is seen that the crystallization exotherm shifts to lower temperatures with increasing cooling rates.

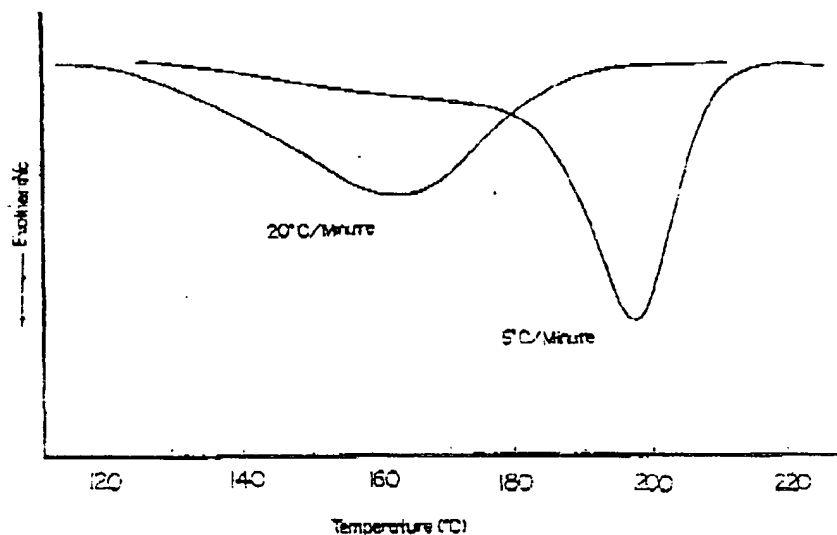


Fig. 5.6 Crystallization exotherms of PET at various cooling rates

The area under the exotherm is related to the heat of crystallization,  $\Delta H_c$ , as discussed previously. The amount of crystallinity can be calculated from the heat of crystallization. Figure 5.7 gives the variation of  $\Delta H_c$  and the corresponding percent crystallinity of various PET samples as a function of cooling rates.

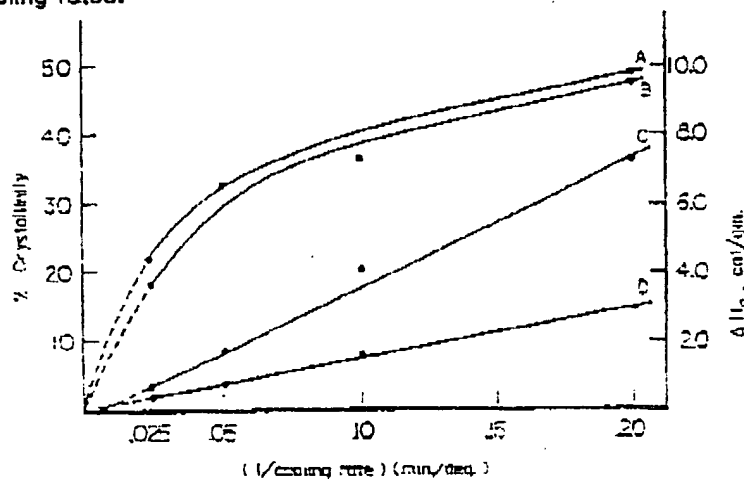


Fig. 5.7 Percent crystallinity, and heat of crystallization as a function of reciprocal of cooling rate for various PET samples. A = Celanese 4070C, 0.7 I.V. B = Goodyear 5737A, 0.7 I.V. & 5041X, 0.8 I.V. C = Goodyear 5041, 1.0 I.V. D = Eastman X-14829-93-1, 0.8 I.V.

These results show dramatic differences in the crystallization behaviors of the various PET resins. The sample D (Eastman 0.8 I.V.) exhibits slower crystallization rates than Sample C (Goodyear 1.0 I.V.) although it is of lower molecular weight. This is attributed to the different catalyst systems used. The effect of the catalyst system is more clearly demonstrated by comparing Curve B (Goodyear 0.8 I.V.) with curve D (Eastman 0.8 I.V.) These samples are of about the same molecular weight but are made by different polycondensation processes employing different catalysts.

The results in Figure 5.7 are important in relation to the cooling required to produce clear parts of PET. Zero percent crystallinity can be achieved when cooling at about 130°C/min. for the resins (D) and (C). At this cooling rate, however, resins represented by curves (B) and (A) respectively exhibit 6 and 9% crystallinity. According to these results, resins represented by curves (A) and (B) require a cooling rate of more than 400°C/min. to produce crystallinity levels of less than 1%.

#### Kinetics of Dynamic Crystallization

The Avrami Equation (3) describing isothermal crystallization has been extended by Ozawa<sup>(8)</sup> for the nonisothermal kinetic process. The modified Avrami equation is given by:

$$1 - a(T) = e^{-K(T)/R^n} \quad (6)$$

where  $a(T)$  is the amount of transformed material at temperature  $T$ ,  $K(T)$  is the rate,  $R$  is the cooling rate, and  $n$  is the Avrami exponent which describes qualitatively the mechanisms of crystallization.

Equation (6) can be used to obtain the kinetic parameters if one observes the crystallization process at different cooling rates, since Eq. (6) can be represented as:

$$\log \{ -\ln(1-a) \} = \log K - n \log R \quad (7)$$

A plot of  $\log \{ -\ln(1-a) \}$  against  $\log R$  at a given temperature should yield a straight line with a slope of  $(-n)$  and an intercept of  $\log K$ . Typical plots of the above equation for the dynamic crystallization behavior of various PET resins are given in Figures 5.8 and 5.9 for Goodyear 5041 and Eastman PET, respectively.